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FIRST OXYGEN FROM LUNAR BASALT

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Introduction. The Carbotek/Shimizu process to produce oxygen from lunar soils has been successfully demonstrated on actual lunar samples in laboratory facilities at Carbotek with Shimizu funding and support. Apollo sample 70035 containing approximately 25 % ilmenite (FeTiO_3) was used in seven separate reactions with hydrogen gas varying temperature and pressure: $\text{FeTiO}_3 + \text{H}_2 \rightarrow \text{Fe} + \text{TiO}_2 + \text{H}_2\text{O}$. The experiments gave extremely encouraging results as all ilmenite was reduced in every experiment. The lunar ilmenite was found to be about twice as reactive as terrestrial ilmenite samples. Analytical techniques of the lunar and terrestrial ilmenite experiments performed by NASA Johnson Space Center include iron Mossbauer spectroscopy (FeMS), optical microscopy, SEM, TEM, and XRD. The Energy and Environmental Research Center at the University of North Dakota performed three SEM techniques (point count method, morphology determination, elemental mapping), XRD, and optical microscopy.

Experimental. 10.000 grams of lunar sample 70035 were obtained from NASA for this experimental work. The sample contains pyroxene, ilmenite, plagioclase, and minor olivine. The basalt was crushed in a nitrogen blanketed glove box using a mortar and pestle and exhibited a surface/volume mean particle diameter of about 240 microns. Reduction with hydrogen proceeded in seven tests at temperatures of 900-1050°C and pressures of 1-10 atmospheres [1]. A capacitance probe, measuring the dew point of the gas stream, was used to monitor the reaction.

Reaction Kinetics and Implications. Reduction of the lunar basalt was extremely rapid, with major evolution of water occurring within minutes after the introduction of hydrogen. The data were best represented by a shrinking-core process in which both chemical reaction and diffusion play significant roles. Reaction rate showed only a 0.15-order dependence on hydrogen concentration. Rate and diffusion constants were such that, at comparable conditions of 1000°C and 10 atm., lunar ilmenites were initially about twice as reactive as the pure terrestrial ilmenites. The reduction of terrestrial MLS-1 basalt by hydrogen at 1100°C was also rapid, with major evolution of water occurring within minutes after the introduction of hydrogen.

In comparison to pure terrestrial ilmenite, the lunar sample reactivity starts out much higher than the terrestrial sample and falls much more steeply with time. This difference in reactivity behavior has important implications for both kinetic and reactor modeling as it affects both residence time and reactor sizing. It also indicates the inadequacy of relying solely on simulant materials for this type of research.

The resulting implications for a lunar oxygen plant can be determined. The predicted maximum output from a lunar oxygen plant is directly proportional to the ilmenite content of the feedstock. Most lunar rocks and soils that contain FeO and TiO_2 have essentially all titanium present as part of the ilmenite. Thus ilmenite abundance is proportional to the sample's titanium content. The expected oxygen yield is equal to 20 wt% of the feedstock's TiO_2 content assuming only FeO in ilmenite is reduced. Based on abundances of TiO_2 in representative Apollo basalt and soil samples, a lunar plant using the hydrogen reduction process would require about 40 tons of high-titanium regolith feedstock to produce each ton of oxygen [2].

Solid Sample Analysis. Ilmenite The FeMS spectrum of unreacted lunar basalt 70035 contains doublet peaks characteristic of ilmenite and pyroxene, the two major iron-bearing phases. The spectrum of the 900 °C sample (Figure 1) shows the sextet of peaks characteristic of iron metal, along with the pyroxene doublet. The ilmenite peaks are not detectable, indicating essentially complete reduction of the Fe^{2+} in this mineral. This was the case for all reacted lunar samples.

All of the reacted ilmenite grains examined by optical microscopy and SEM display characteristic phase separation textures. Ilmenite in the 900 °C sample contains generally parallel stringers of iron metal approximately 1 micrometer wide and tens of micrometers in length, in a matrix of titanium oxide

(Figure 2). The texture is uniform from the edge to the center of each grain. Samples reacted at 1000 and 1050 °C feature slightly wider and less regular stringers, along with clusters of submicrometer iron blebs. These samples commonly show iron metal concentrated on grain surfaces. From SEM photographs, the porosity of iron metal and titanium oxide from reduced ilmenite was estimated at 21%. This compares very well with values calculated from the density differences between ilmenite, Fe, and TiO₂ products.

Titanium Oxide The reduction of ilmenite yields iron metal plus a residue of TiO₂. In fact, the latter phase can also be reduced under suitable conditions. The reduction of TiO₂ involves a series of suboxides with the general formula Ti_nO_{2n-1}, known as magneli phases. The phase produced in a given reaction is a sensitive function of temperature and oxygen fugacity.

X-ray diffraction patterns of the reduced lunar samples show no detectable TiO₂, but do include peaks attributable to titanium suboxides. Phases include Ti₇O₁₃, Ti₆O₁₁, and Ti₄O₇. High-resolution TEM analysis of the 1050 °C sample confirms the epitaxial intergrowth of a disordered combination of Ti₆O₁₁ and more reduced titanium oxides.

Pyroxene The major iron-bearing phases in lunar basalt 70035 are the clinopyroxenes augite (Ca₃₇Mg₄₇Fe₁₆) and pigeonite (Ca₇Mg₆₄Fe₂₉). The FeMS spectra of both the starting lunar basalt and the reacted samples are dominated by the pyroxene doublet. The majority of iron atoms in pyroxene within the reacted samples thus remain in the ferrous oxidation state, while most of the iron metal was derived from reduction of ilmenite.

Evidence of limited pyroxene reduction is present in the analytical data, however. The FeMS spectrum of unreacted lunar basalt shows 23% of the total peak area occupied by ilmenite and 77% by pyroxene. The spectrum of the 900 °C sample (Figure 1) shows 36% of the total peak area occupied by the iron metal sextet and 64% by pyroxene. This decrease in the relative total area of the pyroxene peaks is qualitative evidence that a portion of the Fe²⁺ in the pyroxene of this sample was reduced to iron metal. Again, this reduction is sensitive to temperature and hydrogen-to-water ratio.

Olivine Olivine crystals in high-Ti Apollo 17 basalts have FeO concentrations of 27-28 wt% (Fa₃₀₋₃₂). The abundance of olivine in sample 70035 is too low to permit its detection by either FeMS or XRD. The SEM images of rare olivine grains, however, show evidence of small-scale phase separation. Olivine crystals display scattered submicrometer iron blebs on exterior surfaces and narrow iron-filled veins and cracks extending tens of micrometers into the interiors.

Plagioclase Lunar anorthite generally contains less than 1 wt% FeO. No change in this mineral in any of the reacted lunar basalt samples was observed. The XRD peak positions are unchanged from those of the starting basalt. None of the SEM images shown any sign of phase separation nor decoration of plagioclase grains with iron metal.

References. [1] Ness, R. O., Jr., L. L. Sharp, D. W. Brekke, C. W. Knudsen, and M. A. Gibson (1992) in *Engineering, Construction and Operations in Space III*, Am. Soc. Civil Eng., New York, pp. 617-628. [2] Allen, C. C., M. A. Gibson, C. W. Knudsen, H. Kanamori, R. V. Morris, L. P. Keller, and D. S. McKay (1992) in *Workshop on Geology of the Apollo 17 Landing Site*, Lunar and Planetary Institute, Houston, pp. 1-2.

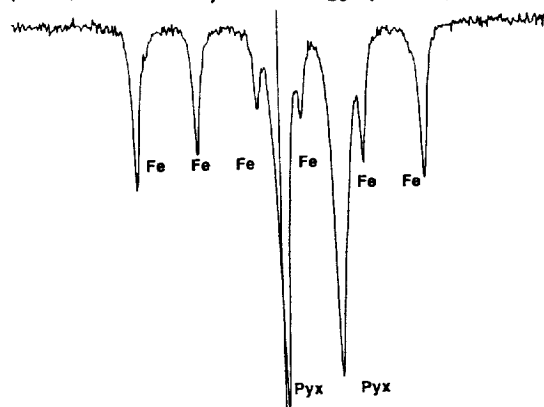


Fig. 1 FeMS spectrum of lunar basalt 70035 reacted at 900°C. Fe = iron metal
Pyx = pyroxene

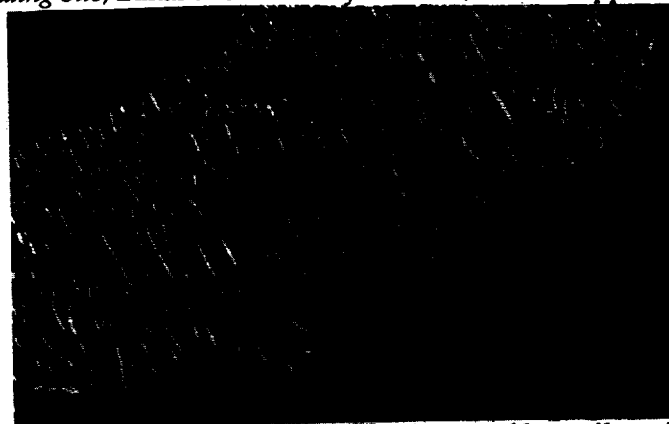


Fig. 2 Back-scattered electron SEM image of lunar ilmenite grain reacted at 900°C. Bright stringers of iron metal are set in darker titanium oxide. Frame width = 350 µm.